



Analysis of dioxins by GC-TQMS

KEY WORDS: TQMS, dioxins, regulatory standards, MRM

INTRODUCTION

Dioxins refers to polychlorinated dibenzo-p-dioxins (PCDDs) and related compounds polychlorinated dibenzofurans (PCDFs) also called as "furans" (Figure 1). These two groups of compounds are among the most toxic chemicals and are classified as Persistent Organic Pollutants (POPs).

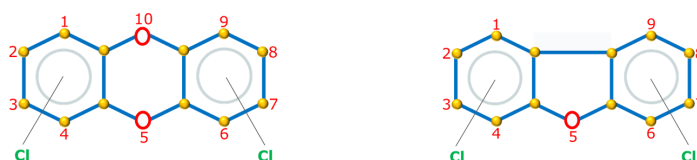


Figure 1. Dioxins and Furans

Dioxins are anthropogenic compounds produced unintentionally as by-products in some industrial activities and waste combustion processes, mainly. In addition to be present in the environment, dioxins are fat-soluble and bio-accumulative compounds in the tissues of animals and humans. Consumption of food is the more important exposure for humans, in particular, fish, shellfish, dairy products and meat.

Dioxins can invoke serious health effects in humans such as loss of body weight, hormone disruption, reproductive disorders, skin toxicity, immune system disorders and cancer, among other diseases. Since 2014, GC-MS/MS is an EU-accepted technique as confirmation method for dioxin analysis in accordance with EU 589/2014 and subsequent regulations implemented in this regard.



Figure 2. SCION Instruments 8300 GC coupled to a 8900 TQMS with a 8400 Autosampler

SCION 8300 GC	
Carrier gas	Helium, 1.5 mL/min, constant flow
Injector	1177 split/splitless, 280 °C
Injection volume	1 µL, pulsed splitless
Insert	4 mm ID fritted liner
Column	BR-Dioxins, 60m x 0.25mm, 0.25 micron film thickness
Column temp.	140 °C, hold 1 min→200 °C at 20 °C min. hold 1min→320 °C at 5 °C/min hold 14 min,
Autosampler	SCION 8400
8900 GC-TQMS	
Source	EI, 280°C
X-line temp.	280 °C
Collision gas	Ar, 1.5 mTorr
MS mode	Dynamic MRM
Scan time	Automatic, EDR
Quad resolution	Q1=0.7 mass unit, Q3= 0.7 mass unit
Software	Compass TQ

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RESULTS AND DISCUSSION

The SCION instruments 8900 TQMS is capable of resolving the different classes of dioxins using the power of MRM (Figure 3). Further, the power of the 8300 GC is evidenced by the chromatographic resolution of the HxCDF isomers, well below the 25% peak to peak separation stipulated in the regulations for quantification (Figure 4).

The inclusion of stable isotope labelled internal standards is a key part of the regulatory framework. The Compass TQ software package for automatic quantitation allows a fast and easy overview of the results. Users can set an extensive number of evaluation rules to meet any stringent analytical regulation. These rules are applicable to any compound in the method and values can be customized by compound.

RQ	Score	RT Score	Ions Score
1	+++	++	++
2	+++	++	++
3	+++	++	++
4	+	++	+
5	+	++	+
6	+	++	+
7	---	++	---
8	---	++	---

Figure 5. Easy visualisation of scoring

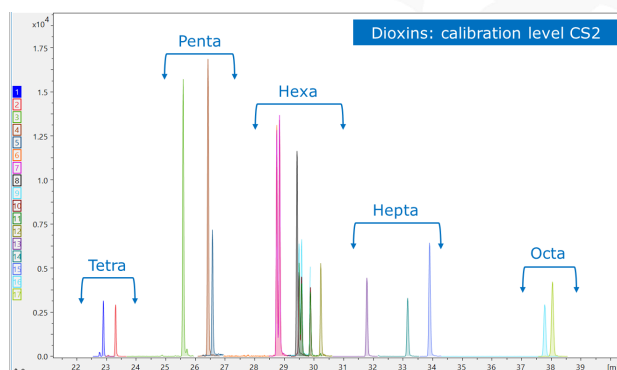


Figure 3. MRM resolution of dioxin classes

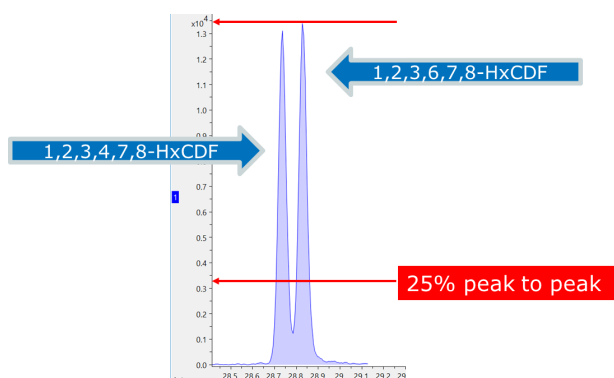


Figure 4. Chromatographic resolution of dioxin isomers

All analytical performance criteria described in EU 644/2017 have been included in the method. If the reported values are higher than the setpoint, software will trigger a red flag to warn user that the compound needs to be reviewed (Figure 5).

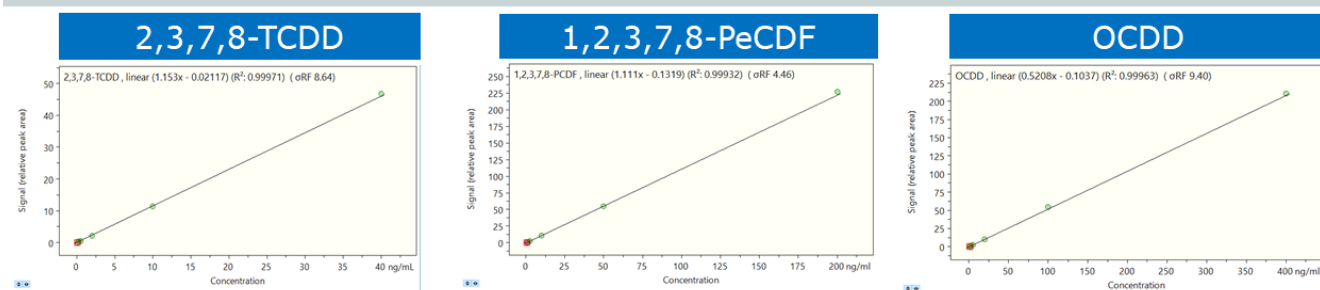


Figure 6. Linearity of response

The calibration curves (Figure 6) yielded a R^2 value > 0.99 with a RSD of $< 13\%$. Retention time drift was low ($< \pm 0.1$ m) with recovery ranging from 94-107%.

To experimentally determine signal-to-noise ratio (s/n), the lowest calibration level CSL was diluted 10-fold and 20-fold with n-nonane. $1\mu\text{L}$ of each was injected. Both ions (quan+qual) were detected at LOQ (10fg) and LOD (5fg) levels.

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ANALYSIS OF FLY ASH

To validate the method, several commercially available certified reference materials were analyzed. Reference materials were split in two aliquot parts: one analyzed by 8900 GC-TQMS and the other sent to an external laboratory for analysis by GC-HRMS.

One such comparative analysis was of fly ash (Certified material BCR-615). The data (Table 3, Figure 7) showed an accuracy of $\pm 20\%$ with good correlation between the HRMS and TQMS results.

DETERMINATION OF DIOXINS IN ANIMAL FEED

To check performance of the method in real samples, an animal feed sample was doped with dioxins at very low levels. Recovery rates of stable isotope labelled internal standards was 60-120%. For every analysis, Compass TQ software checks ion ratios tolerance (RQ score) for each target compound allowing the user to have confidence in compliance with regulatory standards. Ion ratio QC was found to have a tolerance of $\pm 15\%$. Figure 8 shows the stability of the ion ratios for 2,3,7,8-TCDD once the complete batch performed for calibration standards and samples is completed.

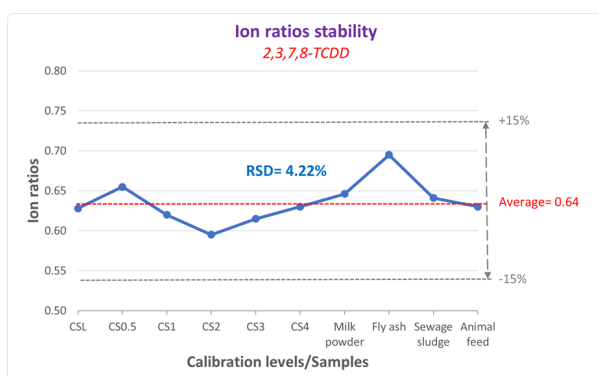


Figure 8. Stability of ion ratios across sample set

Table 3. Results of key compound quantification by HRMS and TQMS compared to certified values

Compound	Certified value (ng/Kg)	GC-HRMS (ng/Kg)	GC-MS/MS (ng/Kg)
2,3,7,8-TCDD	27	31.5	25.8
1,2,3,7,8-PeCDD	92	97.5	108.6
1,2,3,4,7,8-HxCDD	74	69.9	70.7
1,2,3,6,7,8-HxCDD	103	100.4	100.9
1,2,3,7,8,9-HxCDD	108	104.7	89.0
1,2,3,4,6,7,8-HpCDD	870	845.6	885.4
OCDD	1750	1907.5	2037.0
2,3,7,8-TCDF	86	93.3	85.2
1,2,3,7,8-PeCDF	176	162.5	156.7
2,3,4,7,8-PeCDF	125	129.7	111.3
1,2,3,4,7,8-HxCDF	203	185.4	189.6
1,2,3,6,7,8-HxCDF	204	204.1	182.3
1,2,3,7,8,9-HxCDF	13.3	9.6	11.2
2,3,4,6,7,8-HxCDF	130	170.6	151.4
1,2,3,4,6,7,8-HpCDF	750	703.8	723.0
1,2,3,4,7,8,9-HpCDF	61	66.4	61.1
OCDF	290	274.7	318.3

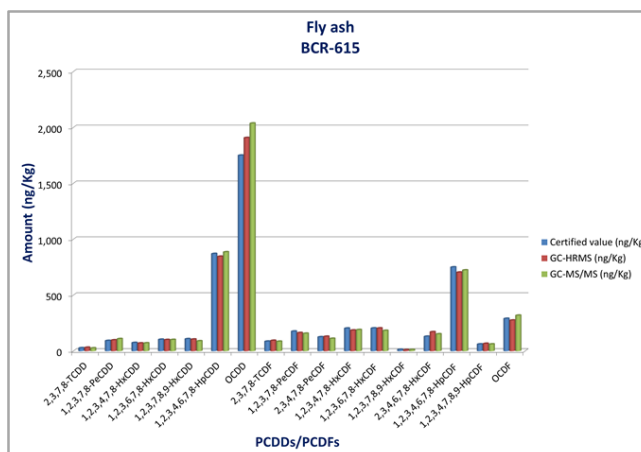


Figure 7. Correlation of HRMS, TQMS and certified values

CONCLUSION

Analytical performance obtained with 8900 GC-TQMS demonstrate that this is a powerful instrument to analyze dioxins in food, feed and environmental samples with confidence. High selectivity with specific MRM transitions in addition to extensive QC parameters allows unambiguous identification and confirmation of dioxins avoiding false positives/negatives. Superb sensitivity at lower femtogram on-column level equivalent to low pg/g -TEQ levels in original samples, injecting a small sample volume (1 μ L).

SCION Instruments

UK

Netherlands

4 Michaelson Square,
Livingston, EH54 7DP,
Scotland, UK
Phone +44 (0) 1506 300 200

The

Amundsenweg 22-24,
4462 GP Goes,
The Netherlands
Phone +31 (0) 113 287 600